

## OPERATING EXPERIENCE WITH THE INTEGRATED DRY NO<sub>x</sub>/SO<sub>2</sub> EMISSIONS CONTROL SYSTEM

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### INTRODUCTION

This paper presents the results to date from the Public Service Company of Colorado (PSCC), U. S. Department of Energy (DOE), and Electric Power Research Institute (EPRI), sponsored Integrated Dry NO<sub>x</sub>/SO<sub>2</sub> Emissions Control System project. This DOE Clean Coal Technology III demonstration project is being conducted at PSCC's Arapahoe Generating Station Unit 4, located in Denver, Colorado. The Integrated Dry NO<sub>x</sub>/SO<sub>2</sub> Emissions Control System consists of five major control technologies that are combined to form an integrated system to control both NO<sub>x</sub> and SO<sub>2</sub> emissions. NO<sub>x</sub> reduction is obtained through the use of low-NO<sub>x</sub> burners, overfire air, and urea-based Selective Non-Catalytic Reduction (SNCR), while dry sorbent injection using either sodium- or calcium-based reagents with humidification is used to control SO<sub>2</sub> emissions. The project goal is to provide up to a 70% reduction of both NO<sub>x</sub> and SO<sub>2</sub> emissions. The combustion modifications were expected to reduce NO<sub>x</sub> by 50% with the expectation that the SNCR system would provide the remaining 20% reduction. Dry Sorbent Injection was expected to provide 50% removal of the SO<sub>2</sub> emissions while using calcium-based reagents. As sodium is much more reactive than calcium, it was expected to provide SO<sub>2</sub> removals of up to 70%.

### UNIT DESCRIPTION

Arapahoe Unit 4 is a 100 MWe down-fired boiler which was built in the early 1950's, and was designed to burn Colorado lignite or natural gas. Currently, the main fuel source is a Colorado low-sulfur (0.4%) bituminous coal. The original firing configuration consisted of 12 intertube burners located on the roof of the furnace. Each burner consisted of a rectangular coal/primary air duct which was split into 20 separate nozzles that injected the coal/air mixture evenly across the furnace roof. Secondary air was injected around each of the individual coal nozzles, and there were no provisions to control the rate of fuel and secondary air mixing. Baseline NO<sub>x</sub> levels for this boiler ranged from approximately 780 to 840 ppmc (ppm, dry corrected to 3% O<sub>2</sub>), depending on load. Arapahoe Unit 4 uses a fabric filter dust collector for particulate control.

### SYSTEM DESCRIPTION

Babcock & Wilcox (B&W) provided the low-NO<sub>x</sub> burners and overfire air system for the Arapahoe Unit 4 project. B&W's DRB-XCL® (Dual Register Burner - axially Controlled Low-NO<sub>x</sub>) burner had been successfully used to reduce NO<sub>x</sub> emissions in wall-fired boilers, but had never been used in a vertically-fired furnace. The burner features dual spin vane registers which allow control of the swirl imparted to the secondary air in both the inner and outer regions of the flame. These registers provide a great amount of control over the rate of combustion, and thus the amount of NO<sub>x</sub> formed. The burners also feature a sliding air damper which allows the total secondary air flow to be controlled independently of the spin vane setting. In many older burner designs, a single register is used to control both the total secondary air flow and the rate of air/fuel mixing.

While low-NO<sub>x</sub> burners alone have proven to be effective for reducing NO<sub>x</sub>, combustion staging can further reduce NO<sub>x</sub> emissions. Overfire air delays combustion by redirecting a portion of the secondary air to a region downstream of the main combustion zone. Three B&W Dual-Zone NO<sub>x</sub> ports were added to each side of the furnace approximately 20 feet below the boiler roof. A numerical modeling study was performed by B&W in order to determine the optimum size and location for the ports. As a result, the NO<sub>x</sub> ports were not spaced symmetrically across the furnace side walls. The ports were also designed to inject up to 25% of the total secondary air through the furnace sidewalls. The dual-zone NO<sub>x</sub>

ports separate the overfire air into two regions. The outer zone features adjustable spin vane registers which disperse air in the region near the wall. The center zone produces an air jet with sufficient momentum to penetrate deep into the furnace. The two-stage injection provides faster mixing and more equal distribution of overfire air into the furnace.

NOELL, Inc. designed and supplied the urea-based SNCR system for the Arapahoe Unit 4 project. The disadvantage of urea injection, as with any SNCR chemical, is that the process operates over a very narrow temperature window. If the temperature is too high, the urea can be converted to  $\text{NO}_x$ . If the temperature is too low,  $\text{NO}_x$  removal efficiencies are reduced, and the emissions of unreacted chemical (ammonia slip) increases. The system at Arapahoe Unit 4 uses NOELL's proprietary dual-fluid injection nozzles to distribute the chemical uniformly into the boiler. A centrifugal compressor is used to supply a large volume of medium pressure air to the injection nozzles to help atomize the solution and rapidly mix the chemical with the flue gas. Two levels of injection nozzles were installed in order to provide the capability to follow the optimum temperature window as its location within the boiler changed with load. A cold-flow modeling study and detailed furnace exit gas temperature measurements were performed in order to determine the optimum location of the two injection levels.

Prior to the installation of the low- $\text{NO}_x$  combustion system, a short test program was conducted to assess the performance of the urea-based SNCR system with the original burners. Early tests at the cooler Level 2 injection location showed the region to be too cold for urea injection, even at full load. Subsequent temperature measurements revealed that the furnace exit gas temperatures were significantly lower (on the order of 150 to 200°F) than those measured previously. Although the reason for the decrease in temperature could not be conclusively identified, it required that the remainder of the test effort be focused on the hotter Level 1 injection location. During the Level 1 tests, it was found that  $\text{NO}_x$  reductions at low load were somewhat less than expected. Recent full-scale SNCR tests<sup>(1)</sup> have shown that aqueous ammonia ( $\text{NH}_4\text{OH}$ ) can provide increased system performance compared to that for urea in certain temperature ranges. A short term test using aqueous ammonia achieved greater  $\text{NO}_x$  reduction than urea at low load. These results made it desirable to investigate  $\text{NH}_4\text{OH}$  injection in more detail during the SNCR tests scheduled after the low- $\text{NO}_x$  combustion system retrofit. However, due to safety concerns, it was preferable to store urea rather than  $\text{NH}_4\text{OH}$  on-site. To this end, NOELL, Inc. designed and installed a system that allows on-line catalytic conversion of urea into ammonia compounds.

A combination of dry technologies is used at Arapahoe Unit 4 to reduce  $\text{SO}_2$  emissions. PSCC designed and installed a dry sorbent injection system that can inject either calcium- or sodium-based reagents into the flue gas upstream of the fabric filter. The reagent is fed through a volumetric feeder into a pneumatic conveying system, and then into a pulverizer where the size of the material can be reduced to approximately 90% through 400 U.S. Standard mesh. The material is then injected evenly into the duct at a point approximately 100 feet upstream of the fabric filter. A bypass can also be installed to convey the calcium-based reagents into the flue gas upstream of the economizer in a region where the temperature is approximately 1000°F.

While significant  $\text{SO}_2$  reductions can be achieved with sodium-based reagents, calcium hydroxide is less reactive. In order to improve  $\text{SO}_2$  removals with calcium hydroxide, a humidification system was installed in the duct upstream of the fabric filter. The system was designed by B&W and consists of 84 I-jet humidification nozzles which can inject up to 80 gpm of water into the flue gas stream. The system was designed to achieve a 20°F approach to saturation at full load conditions.

## RESULTS

Fossil Energy Research Corporation is conducting all testing of the Integrated Dry  $\text{NO}_x/\text{SO}_2$  Emissions Control System. Currently, the individual testing of the low- $\text{NO}_x$  burners, overfire air, urea injection, calcium duct injection, and calcium economizer injection has been completed. Sodium duct injection testing has started and will continue through January 1994. Testing of the complete

integrated system will continue through mid-1994 with up to four weeks of testing on a high sulfur (2.5%) coal. Although all data have not been reviewed, some preliminary results of the individual technologies comprising the Integrated Dry  $\text{NO}_x/\text{SO}_2$  Emissions Control System will be presented.

**COMBUSTION MODIFICATIONS.** Figure 1 shows the original baseline  $\text{NO}_x$  emissions compared to the post-combustion retrofit emissions, both with and without the SNCR system in operation. The combination of low- $\text{NO}_x$  burners and overfire air alone resulted in  $\text{NO}_x$  reductions varying from 63 to 69% across the load range. The post-retrofit results shown in the figure are for the maximum staging (i.e., maximum overfire air) configuration. In this configuration, approximately 25% of the secondary air is introduced through the  $\text{NO}_x$  ports at full load. It was not possible to reduce the overfire air flow to zero as the ports are located in a very hot section of the furnace and, therefore, require a minimum amount of air flow to assure adequate cooling. These  $\text{NO}_x$  port cooling requirements limited the minimum overfire air flow to approximately 15% of the total secondary air at full load. Tests at the minimum overfire condition indicate that the low- $\text{NO}_x$  burners are responsible for the majority of the  $\text{NO}_x$  reduction over the range of overfire air flow rates tested, as the removals increase only 10% as overfire air is increased from 15 to 25% at full load. At 80 MWe, where the overfire air flow can be reduced to 8% of the secondary air before  $\text{NO}_x$  port temperatures become a concern, the increase in  $\text{NO}_x$  reduction was only 8% as the overfire air was increased from 8 to 25%. However, it must be noted that it was not possible to totally separate the effects of the low- $\text{NO}_x$  burners and overfire air system, since the overfire air flow could not be reduced to zero.

Flyash unburned carbon levels measured after the retrofit were unchanged from the baseline levels, and did not appear to be greatly affected by the amount of overfire air. CO emissions were also comparable to the baseline levels with maximum overfire air, and tended to increase as overfire air flow was reduced to the minimum values. This was not expected, as low- $\text{NO}_x$  combustion retrofits have been known to result in increases in flyash unburned carbon levels and CO emissions. It is hypothesized that this behavior is due to the penetration and mixing of the overfire air in this down-fired configuration. It is also possible that the lack of an effect on flyash unburned carbon is partially due to the reactive nature of the Western coal utilized by the Arapahoe station. This reactivity allows flexibility in operation of the low- $\text{NO}_x$  burners and overfire air system without resulting in increases in unburned carbon levels. However, as mentioned above, CO emissions were found to be sensitive to changes in combustion system operating parameters.

**SELECTIVE NON-CATALYTIC REDUCTION.** Figure 1 also shows the  $\text{NO}_x$  emissions attainable when operating the SNCR system at urea injection rates which limit  $\text{NH}_3$  slip at the fabric filter inlet to 10 ppm. The  $\text{NO}_x$  removals (measured relative to the 240 to 280 ppmc post-retrofit levels) range from 7 to 45% over the load range of 60 to 110 MWe, respectively. The temperature-sensitive nature of the urea injection process and the limitation of only a single usable injection level is apparent in that the  $\text{NO}_x$  removals for a fixed  $\text{NH}_3$  slip level are much lower at the reduced loads where the flue gas temperature is also reduced. The reduction in  $\text{NO}_x$  emissions due to the combined affects of the low- $\text{NO}_x$  combustion system retrofit and SNCR range from 66 to 82% over the load range of 60 to 100 MWe.

While urea injection allowed reasonable levels of  $\text{NO}_x$  removal at higher loads, it was not very effective at reduced loads. A third set of temperature measurements revealed that the low- $\text{NO}_x$  combustion system retrofit resulted in another decrease in furnace exit gas temperatures (this one on the order of 180 to 240°F). In an effort to increase low-load removal, the urea injection system was modified with an on-line ammonia conversion system. This system converts urea to liquid ammonia compounds immediately before injection into the boiler. As ammonia reacts faster than urea and in a lower temperature window, it was expected to provide higher  $\text{NO}_x$  removal at lower loads. The results (Figure 2) showed that, when injected into the same location in the Arapahoe Unit 4 boiler, converted urea provided higher  $\text{NO}_x$  removals than urea when compared on an equal ammonia slip basis. However, the increased  $\text{NO}_x$  removals with converted urea required higher chemical injection rates (ranging from 67 to 133% higher than those for urea injection

at the same load). Therefore, at loads of 80 MWe and greater, urea was the most efficient of the two chemicals.

In addition to creating unwanted ammonia emissions, SNCR can increase nitrous oxide ( $N_2O$ ) emissions.  $N_2O$  emissions with converted urea were lower than those for urea. For converted urea, the fraction of NO reduced which was converted to  $N_2O$  ranged from 3 to 8%, depending on load for a stoichiometric (N/NO) ratio of 1.0. With urea, the conversion ranged from 29 to 35% at a similar chemical injection rate. The  $N_2O$  conversion with urea injection was much higher than that seen before the low- $NO_x$  combustion system retrofit (11 to 16% at a N/NO ratio of 1.0). It is likely that the increase is due to the reduction of the flue gas temperatures in the injection region seen after the retrofit.

**DRY SORBENT INJECTION WITH CALCIUM HYDROXIDE ( $Ca(OH)_2$ ).** Testing of the dry sorbent injection system with  $Ca(OH)_2$  consisted of two phases: duct injection with humidification and economizer injection without humidification. All testing to date has been with a low-sulfur coal and baseline  $SO_2$  emissions in the range of 400 ppmc.

The results of the duct injection tests with humidification at a stoichiometric (Ca/S) ratio of 2.0 are shown in Figure 3. The maximum  $SO_2$  removal of 44% was obtained during a short-term test with the humidification system operating at a 20°F approach to saturation. Immediately after this test, problems developed with the dry flyash transport system, and it is suspected that the low approach temperature operation contributed to the problem. More recently, problems with increased pressure drop across the fabric filter, and deposit build up on the bags occurred after operating the humidification system at a 30°F approach temperature. Currently, studies are still ongoing to determine if these problems were due to steady state operation at the 30°F approach temperature or transient conditions during load changes. At this higher approach temperature,  $SO_2$  removal is reduced to a range of 26 to 36% at a Ca/S ratio of 2.0.

$SO_2$  removals with  $Ca(OH)_2$  injection at the economizer have been much lower than expected. At a Ca/S ratio of 2.0 without humidification,  $SO_2$  removals ranged from 5 to 8%. It was found that distribution of the sorbent with the original injection nozzles was very poor, and only approximately one-third of the flue gas was being treated. Improved nozzles which increased the distribution to approximately two-thirds of the flue gas were installed on one side of the boiler. With the improved distribution,  $SO_2$  removals increased to only 10 to 12% at a Ca/S ratio of 2.0.

**DRY SORBENT INJECTION WITH SODIUM SESQUICARBONATE.** Testing of the dry sorbent injection system with sodium sesquicarbonate ( $NaHCO_3 \cdot Na_2CO_3 \cdot 2H_2O$ ) has just recently begun, and only minimal data is available at this time. Figure 4 shows the  $SO_2$  removals as a function of the stoichiometric injection rate ( $Na_2/S$  ratio) over the range of 0 to 1.5. At a  $Na_2/S$  ratio of 1.4,  $SO_2$  removals of 53 to 63% have been achieved to date. It has been further documented during short-term tests that  $SO_2$  removals in excess of 70% can be achieved at  $Na_2/S$  ratios slightly above 2.0. One byproduct of the dry sodium based  $SO_2$  removal process is the oxidation of NO to  $NO_2$ . This can lead to plume coloration and visibility problems. For instance,  $NO_x$  levels have been seen to increase by 6 to 13 ppm (from a baseline level of 1 to 2 ppm) while injecting sodium sesquicarbonate at Arapahoe Unit 4. One potential synergistic benefit of the Integrated Dry  $NO_x/SO_2$  Emission Control System will be the suppression of the NO to  $NO_2$  oxidation with sodium injection by the  $NH_3$  slip from the SNCR system. These benefits will be documented during future testing of the entire integrated system.

#### CONCLUSIONS

The Integrated Dry  $NO_x/SO_2$  Emissions Control System has been in operation for over one and one-half years and preliminary conclusions are as follows:

- $NO_x$  reduction during baseloaded operation of the unit with the low- $NO_x$  burners and overfire air ranges from 63 to 69% with no increase in flyash unburned carbon levels or CO emissions.

- Low-NO<sub>x</sub> burners provided the majority of the NO<sub>x</sub> reduction, while the overfire air system supplied approximately 8 to 10% additional NO<sub>x</sub> reduction over the range of overfire air flow rates tested.
- Urea injection allows an additional 7 to 45% NO<sub>x</sub> removal with an ammonia slip of 10 ppm at the fabric filter inlet. This increases total system NO<sub>x</sub> reduction to 82% at full load, significantly exceeding the project goal of 70%.
- Higher NO<sub>x</sub> reduction is possible using ammonia compounds as the SNCR chemical, but significantly higher stoichiometric ratios are required at loads of 80 MWe and above. However, it must be noted that the performance of the SNCR system with urea was limited by a large unexpected decrease in furnace exit gas temperature at this particular installation and, therefore, any comparison of the performance of ammonia compounds to that for urea must take this into account.
- N<sub>2</sub>O generation is a potential concern with urea injection, but was greatly reduced when ammonia compounds were injected.
- The maximum SO<sub>2</sub> removal attained during short-term tests with calcium hydroxide injection and duct humidification was 44%.
- Preliminary results indicate SO<sub>2</sub> removals with sodium sesquicarbonate injection in excess of 60%.

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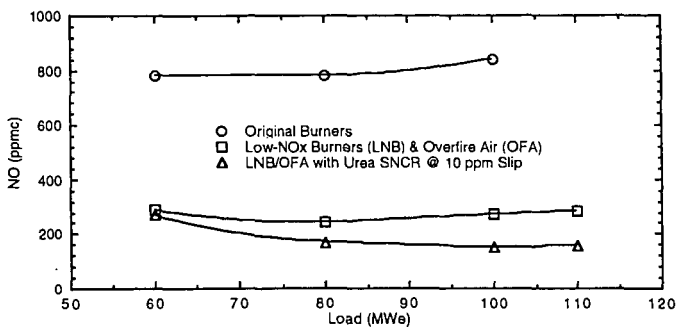


Figure 1. Pre- and Post-Retrofit NO<sub>x</sub> Emissions

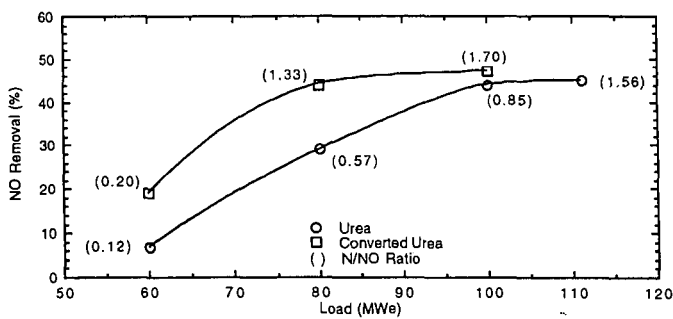


Figure 2. NO<sub>x</sub> Removals for Urea and Converted Urea Injection at a Fixed NH<sub>3</sub> Slip Level of 10 ppm

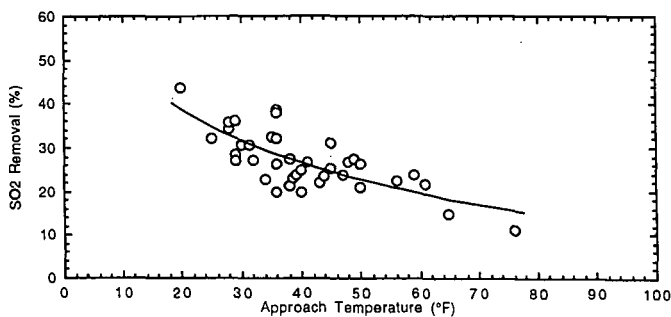


Figure 3. SO<sub>2</sub> Removals with Calcium Hydroxide for Duct Injection with Humidification (Ca/S = 2.0)

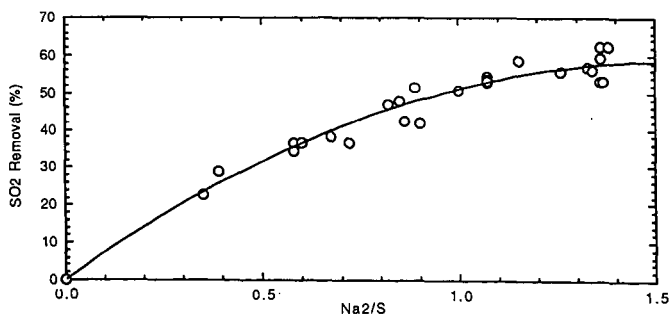


Figure 4. SO<sub>2</sub> Removals with Sodium Sesquicarbonate for Duct Injection without Humidification